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ENDOR STUDIES OF RADIATION-PRODUCED TRAPPED ELECTRONS AND RADIC--ETC(U)

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ENDOR STUDIES OF RADIATION-PRODUCED  
TRAPPED ELECTRONS AND RADICALS IN  
DISORDERED SYSTEMS AND  
RADICAL-MATRIX INTERACTIONS IN  
POLYMERS AND ON SURFACES

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FINAL REPORT

LARRY KEVAN

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) ENDOR has been applied to radiation-produced trapped electrons and radicals in glassy and polymeric matrices. The temperature dependance of peroxy radical spectra has been analyzed in terms of specific motional mechanisms. Abstracts of 20 publications and titles of 40 scientific talks on these topics are given. The emphasis has been to develop new methods for the application of ENDOR to disordered systems and for the analysis of peroxy radical spectra vs temperature.			

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This Final Report covers the period November 1, 1975 to February 28, 1982.

### 1. Brief Progress Summary

During this period we have developed matrix ENDOR (electron nuclear double resonance) for the study of radicals in disordered systems including polymers and have demonstrated the utility of  $g$ -anisotropy averaging of peroxy radicals for the study of specific motional mechanisms in disordered systems.

A generalized matrix ENDOR lineshape model has been developed using a density matrix formalism. The model includes the radiofrequency and microwave field intensities as well as different relaxation paths explicitly. This model has been tested against the small amount of single crystal data that exist for matrix ENDOR responses, namely for the methyl radical in  $\gamma$ -irradiated lithium acetate dihydrate and for the protonated carboxylic anion radical in  $\gamma$ -irradiated L-alanine. In general, the theoretical simulations agree satisfactorily with the experimental lineshape, microwave magnetic field dependence and radiofrequency magnetic field dependence. It is further deduced that an angularly independent nuclear relaxation mechanism dominates the matrix ENDOR response. Further investigation has shown that this angularly independent relaxation rate can be identified with nuclear spin diffusion. This now gives a fairly complete understanding of the matrix ENDOR response.

Matrix ENDOR and ESR have been used to study several  $\gamma$ -irradiated substituted methacrylate lithographic polymers. Mid-chain and end chain radicals are found and ENDOR is used to assess the compactness of the radiation degradation region and hence the potential resolution of the resist.

A theoretical study based on a semicontinuum potential model has also been carried out on ENDOR studies of trapped electrons in hydroxy sugar crystals. The results suggest that dipole rearrangement occurs during electron trapping even at 4 K.

The use of peroxy radicals for motional studies was first developed with the triphenylmethylperoxy radical in  $\gamma$ -irradiated polycrystalline triphenylacetic acid. Temperature dependent ESR studies at 35 GHz gave reversible complex spectra at intermediate temperatures which aroused our interest. It was found possible to stimulate the spectra over the entire temperature range with the modified Bloch equations for motional processes for a specific motional model,  $120^\circ$  jumps of the peroxy group about the C-O bond. However, the most significant finding was the sensitivity of the spectral simulations to the particular motional model assumed. This provides the first spin probe with good specificity for identifying particular motional mechanisms.

In further development of this motional probe we have shown that a similar formalism can be used to interpret the spectra of  $(\text{CO}_2\text{-O}_2)^-$  on an MgO surface in terms of a specific cubic jump motional model of the O-O group. This may reflect the cubic symmetry of the MgO surface and indicates a new method for studying motional processes of oxygen species on surfaces.

Also, the peroxy radical motional probe has been shown to be effective in polymeric systems by a study of peroxy polyethylene in urea-polyethylene complexes. The most recent work explores the applicability of peroxy radical probes to polytetrafluoroethylene, methacrylate polymers, polypropylene, poly(vinylidene fluoride), urea-n-alkane adducts and poly(vinyl alcohol). This comprehensive series of investigations demonstrates the effectiveness of using the peroxy probe for determining specific motional mechanisms in polymers. The general types of motion as a function of position on the polymer chain and as a function of side chain substituent polarity and size have been largely delineated.

## 2. Abstracts of Publications

1. Electron-Proton Distance Changes During Solvation of Electrons in 3-Methylhexane and Other Organic Glasses by Matrix ENDOR and Second Moment EPR Lineshape Analyses, Ding-Ping Lin and Larry Kevan, Chem. Phys. Lett., 40, 517 (1976).

Matrix proton ENDOR signals have been measured for stabilized electrons produced by irradiation at 4K and at 77K in 3-methylhexane glass. The matrix proton ENDOR linewidths are smaller when irradiation is carried out at 77K. This difference is analyzed to show a  $0.15\text{\AA}$  change in the average electron proton distance as the electron produced at 4K is solvated by warming to 77K. Similar distance changes have been deduced from a second moment EPR lineshape analysis for electrons in several organic glasses for which the proton hyperfine interaction is mainly dipolar.

2. Solution ENDOR of the Tri-*t*-butyl Phenoxy Radical: Nuclear Relaxation Mechanisms, P.A. Narayana and Larry Kevan, J. Magn. Resonance, 24, 137 (1976).

ENDOR studies of the tri-*t*-butyl phenoxy radical in mineral oil in the temperature range 300-350K have been carried out to assess the nuclear relaxation mechanisms. The temperature dependence of the ring  $\alpha$ -proton intensities differs markedly from that of the *t*-butyl protons. The results are analyzed in terms of a multi-level model system containing two equivalent  $\alpha$ -protons and three equivalent  $\beta$ -protons employing the full theory developed by Freed and his collaborators including coherence effects. The analysis indicates that the electron nuclear dipolar (END) mechanism is

dominant for the ring  $\alpha$ -protons and that the  $\alpha$ - and  $\beta$ -protons have distinctly different behavior vs temperature. To the extent that the nine t-butyl protons can be approximated by three methyl protons the results suggest that both END and modulation of isotropic hyperfine coupling mechanisms provide comparably important pathways for nuclear relaxation of such protons.

3. Matrix ENDOR Studies of the Orientation of Amine Molecules Around Trapped Electrons in  $\gamma$ -Irradiated Amine Glasses, F.Q.H. Ngo, S. Noda and L. Kevan, Proceedings of Fourth International Symposium on Radiation Chemistry, P. Hedvig and R. Schiller, eds., Akademiai Kiado, Budapest, 1977, pp. 951-962.

Trapped, solvated electrons in primary, secondary and tertiary amine glasses have been studied by EPR and ENDOR to deduce aspects of the geometrical structure of the amines around the electrons. NH deuteration experiments show no effect on the EPR and ENDOR linewidths of trapped electrons in primary and secondary amines and indicate that the alkyl protons are closer than the NH protons to the electron. The trapped electron EPR linewidths are larger in primary and secondary amines ( $\sim 7\text{G}$ ) than in tertiary amines ( $\sim 4\text{G}$ ) which suggests a small contact hyperfine coupling; this is supported by ENDOR data. In tertiary amines EPR and ENDOR results on trapped electrons suggest that the proton interaction is purely dipolar and that the closest protons are  $\sim 3.4\text{\AA}$  from the electron. In the more polar primary and secondary amines the small proton contact interaction suggests that the closest protons are  $< 3.4\text{\AA}$  from the electron.



4. ENDOR and ELDOR of Paramagnetic Species in Disordered Matrices, L. Kevan and P.A. Narayana, Chapter IV, in Multiple Electron Resonance Spectroscopy, M. Dorio and J. Freed, eds., Plenum Press, New York, 1979, pp. 229-259.

The applications of electron nuclear double resonance (ENDOR) and electron-electron double resonance (ELDOR) to radicals trapped in disordered matrices such as glasses and polycrystals are discussed. In polycrystalline matrices single-crystalline ENDOR spectra can be obtained in certain systems. In glassy matrices only a matrix ENDOR Line is usually seen. A simple model for matrix ENDOR has given much semiquantitative information about the delocalization of the unpaired electron wavefunction. An improved model is currently being developed which appears to give a more quantitative picture of the matrix ENDOR response. ELDOR has been used to evaluate the noninteracting spin packet model of inhomogeneously broadened lines and to directly study cross relaxation between two different radicals in glassy matrices.

5. An Improved Lineshape Model for the Matrix ENDOR Response in Disordered Systems, P.A. Narayana, M. K. Bowman, D. Becker, L. Kevan and R.N. Schwartz, J. Chem. Phys., 67, 1990 (1977).

An improved lineshape model for the matrix ENDOR response near the free-nucleus precession frequency in disordered systems is developed and applied to a spin system with  $S=1/2$  and  $I=1/2$  using a density matrix formalism. The model includes the radiofrequency and microwave field intensities as well as different spin relaxation paths explicitly. Application of this model to trapped electrons in 2-methyltetrahydrofuran glass gives geometrical and magnetic data which are in excellent agreement with existing data from electron spin echo experiments. The effects of the various parameters in the theory of the matrix ENDOR lineshape are discussed.

6. Matrix ENDOR Studies of the Proton Environment of the Radical in Natural and Solvent-Refined Coal, S. Schlick, P.A. Narayana and Larry Kevan, J. Am. Chem. Soc., 100, 3322 (1978).

The radical in natural and solvent refined coal (SRC) has been studied by electron nuclear double resonance (ENDOR) between room temperature and 30 K as a function of the microwave and radiofrequency field intensities. The observation of a strong proton matrix ENDOR line show interaction of the coal radical with nearby protons. By simulating the matrix ENDOR line with a new, improved lineshape model we conclude that the closest protons are situated at  $2.6 \pm 0.2 \text{ \AA}$  from the unpaired electron of the coal radical and that the average isotropic hyperfine coupling of these closest protons is  $1.3 \pm 0.3 \text{ MHz}$ . The experimental variation of the matrix ENDOR lineshape and intensity with microwave and radiofrequency field intensity is simulated well at lower microwave powers by the improved ENDOR lineshape model although deviations occur at higher microwave power. The differences of the ENDOR signals for natural and solvent refined coal are explained in terms of different electron and nuclear spin-lattice relaxation times, in line with the rather well established assumption that the structures in both coals are similar.

7. Test of Improved Matrix Endor Lineshape Model Based on Single Crystal Data, L. Kevan, P. A. Narayana, K. Toriyama and M. Iwasaki, Magnetic Resonance and Related Phenomena, Proc. XXth Congress Ampere-Tallinn, USSR; E. Kundla, E. Lippman and T. Salurere, eds., Springer-Verlag, Berlin, 1979, p. 221.

A new general matrix ENDOR lineshape model is tested against data on the  $\text{CH}_3$  in  $\gamma$ -irradiated  $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ . The theoretical simulations agree satisfactorily with the experimental lineshape, microwave magnetic field dependence,  $H_1$ , radiofrequency magnetic field dependence,  $H_2$  and angular dependence of single crystal ENDOR line intensities.

8. General Matrix ENDOR Lineshape Model Applied to the Methyl Radical in Lithium Acetate Dihydrate Using Single Data, L. Kevan, P. A. Narayana, K. Toriyama, and M. Iwasaki, J. Chem. Phys., **70**, 5006 (1979).

A new general matrix ENDOR lineshape model is tested against ENDOR data on the methyl radical in  $\gamma$ -irradiated lithium acetate dihydrate. All parameters in the lineshape model are determined or narrowly limited by experiment. These include the dipolar tensors of all protons within 5 Å of the methyl radical, the microwave and radiofrequency magnetic fields, and the electronic and nuclear spin-lattice and spin-spin relaxation times. The theoretical simulations agree satisfactorily with the experimental lineshape, microwave magnetic field dependence, radiofrequency magnetic field dependence and angular variation of single crystal ENDOR line intensities. The effective nuclear spin-lattice relaxation time is  $\sim 10$  ms at 77 K and seems to be dominated by some angularly independent nuclear relaxation mechanism. The angularly dependent electron-nuclear dipolar interaction is found to be of much less importance for the ENDOR response. It is noted that the angular variation of

ENDOR intensities is an important parameter to assess the nuclear relaxation mechanisms that control the ENDOR response. Data on cw and pulsed matrix ENDOR are compared and found to be similar. It is also shown that a model based on idealized lineshape theory for disordered systems can satisfactorily reproduce matrix ENDOR lineshapes. Both models allow calculation of the relative contributions from angularly independent and dependent ENDOR responses.

9. Study of g-Anisotropy Associated with Molecular Motion in the Triphenylmethylperoxy Radical: An Environmental Probe, L. Kevan and S. Schlick, J. Phys. Chem., 83, 3424 (1979).

ESR spectra of triphenylmethylperoxy radical  $\phi_3\text{COO}^\bullet$  in  $\gamma$ -irradiated polycrystalline triphenylacetic acid  $\phi_3\text{CCOOH}$  were measured at 35 GHz as a function of temperature from 80 K to 290 K. Multiple lines were observed due entirely to g-anisotropy. Principal values of the g-tensor at 80 K are 2.0320, 2.0092 and 2.0035. At 290 K an axial g-tensor is observed with  $g=2.0175$  and 2.0128. At intermediate temperatures new lines appeared in the spectrum. All spectral changes with temperature were reversible. The spectra were interpreted with the modified Bloch equations for motional processes. All salient features over the entire temperature range were well reproduced by a motional model involving  $120^\circ$  jumps of the peroxy group about the C-O bond. The jump rates fit an Arrhenius plot and give an activation energy of 9.2 kJ/mole. The possibility of using the peroxy group as an environmental probe of its motional freedom is discussed and several systems where this may be applicable are given.

10. Interpretation of the ESR Spectrum from a Mobile Peroxide on a MgO Surface, S. Schlick and L. Kevan, J. Chem. Phys., 72, 784 (1980).

It is shown that the reported spectra of  $(\text{CO}_2\text{-O}_2)^-$  on MgO at 77K and room temperature can be reinterpreted in terms of a single radical species undergoing intramolecular rotational motion of the O-O group. The "extra" lines in the spectrum at 77K arise from averaging of g-anisotropy and can be simulated by the modified Bloch equations. These results suggest that peroxy radical motion on surfaces can be used as an environmental probe that may be sensitive to local surface geometry.

11. Matrix ENDOR of the Protonated Carboxylic Anion Radical in  $\gamma$ -Irradiated L-Alanine: Simulation Using a General Matrix ENDOR Lineshape Model and Single Crystal Data, L. Kevan, S. Schlick, K. Toriyama and M. Iwasaki, J. Phys. Chem., 84, 1950 (1980).

The matrix ENDOR line from  $\text{CH}_3\text{CH}(\text{NH}_3^+)\dot{\text{C}}\text{OOH}^-$  radical in  $\gamma$ -irradiated L-alanine powder at 77K was simulated using a generalized matrix ENDOR lineshape theory. The input includes hyperfine coupling constants for all protons in the proximity of the radical site as well as the pure dipolar interaction for more distant protons, microwave and radiofrequency magnetic field magnitudes and nuclear and electron spin lattice and spin-spin relaxation times. Simulated matrix ENDOR lines were tested against experimental lineshapes, linewidths and intensity of the ENDOR response as a function of the radiofrequency magnetic field. The simulated ENDOR response was found to be very sensitive to the value of the nuclear spin-lattice relaxation time and a value of 0.15s satisfactorily reproduces the experimental results.

The relevant conclusion from this study is that an angularly independent nuclear relaxation mechanism dominates the ENDOR response.

12. Interpretation of Temperature Dependent ESR Spectra of Peroxy Polyethylene Radicals in Urea-Polyethylene Complex, S. Schlick, and L. Kevan, J. Am. Chem. Soc., 102, 4622 (1980).

Temperature dependent ESR spectra of peroxy polyethylene radicals in urea-polyethylene complexes are successfully simulated by the modified Bloch equations in terms of g-anisotropy averaging of one radical. The motional model that averages the g-tensor corresponds to  $180^\circ$  rotational jumps of the O-O fragment around the C-O bond. An activation energy of 16.1 kJ/mole is derived for this motion. A comparison of peroxy with nitroxide spin probes in polyethylene show that the peroxy probe is more sensitive to the particular motional model that controls the dynamics.

13. The Importance of Nuclear Spin Diffusion As An Angularly Independent Relaxation Mechanism Controlling the Matrix ENDOR Response of Radicals in Molecular Crystals, S. Schlick, L. Kevan, K. Toriyama and M. Iwasaki, J. Chem. Phys., 74, 282 (1981).

In the generalized matrix ENDOR lineshape model [P. A. Narayana et al., J. Chem. Phys., 67, 1980 (1977)] the ENDOR intensity is controlled by the nuclear spin lattice relaxation rate formulated as an angularly dependent intrinsic bulk nuclear relaxation contribution. Comparison of this model with single crystal data [L. Kevan et al., J. Chem. Phys., 70, 5006 (1979)] showed that the angularly independent relaxation rate must be more rapid than the intrinsic bulk nuclear relaxation rate. Here we identify the angularly independent relaxation rate with nuclear spin diffusion and apply this interpretation quantitatively to data on methyl radicals in lithium acetate dihydrate crystals and to the radiation generated  $\text{CH}_3\text{CH}(\text{NH}_3^+) \dot{\text{C}}\text{OOH}^-$  radical in alanine at 77K.

14. Application of the Semicontinuum Potential Model to Deduce Localized Electron Trapping Sites in Single Crystals of D-Sorbitol, L. Kevan, S. Schlick, P. A. Narayana and Da Fei Feng, J. Chem. Phys., 75 1980 (1981).

The semicontinuum model of electron solvation (J. Am. Chem. Soc., 1976, 95, 1398) has been used to calculate the stability of the trapped electron in single crystals of D-Sorbitol at 4.2 K. Experimental ENDOR results suggest an environment of two OH dipoles, with the protons at equal distances from the electron. The geometry of the most probable site in a lattice undistorted by irradiation result in a unbound electron state. This arises because the dominant term in the total energy is the dipole-dipole interaction which is attractive for that geometry. If the oxygen atoms remain fixed at crystal lattice positions but the protons are allowed to rearrange so as to point towards the electron, a minimum in the total energy is obtained, but the electron-proton distance is much shorter than the experimental value. However, good agreement with experiment is obtained for configurations of two or four OH dipoles pointing towards the trapped electron when lattice rearrangement is allowed. These calculations suggest that dipole rearrangement occurs during electron trapping in single crystals even at 4.2K.

15. Study of  $\gamma$ -Irradiated Lithographic Polymers by Electron Spin Resonance and Electron Nuclear Double Resonance, S. Schlick and L. Kevan, J. Appl. Poly. Sci., 27, 319 (1981).

The room temperature gamma irradiation degradation of the lithographic polymers, poly(methylmethacrylate) (PMMA), poly(methyl-

$\alpha$ -chloroacrylate) (PMCA), poly(methyl- $\alpha$ -fluoroacrylate) (PMFA) and poly(methylacrylonitrile) (PMCN), have been studied by electron spin resonance and electron nuclear double resonance (ENDOR) to assess their molecular degradation processes of relevance to electron beam lithography. Two classes of radicals are found, chain radicals and chain scission radicals. PMMA and PMCA mainly form chain scission radicals consistent with degradation while for PMCN the resolution is poorer and this is only probable. PMFA forms mainly chain radicals consistent with predominant crosslinking. The total radical yield is greatest in PMCA and PMCN. ENDOR is used to assess the compactness of the radiation degradation region for PMMA and PMCA and hence the potential resolution of the resist; this appears to be about the same for these methacrylate polymers.

16. Peroxy Radical Probe For Motion In Polytetrafluoroethylene Chains, D. Suryanarayana and L. Kevan, J. Am. Chem. Soc., 104, 668 (1982).

The temperature dependences in the Q-band electron spin resonance (ESR) spectra of mid-chain and end-chain peroxy radicals in  $\gamma$ -irradiated polytetrafluoroethylene are investigated experimentally and theoretically using modified Bloch equations. Computer simulations are carried out for the following motional models; cubic jump, C-O bond rotation ( $120^\circ$  and  $180^\circ$  jumps), and chain axis rotation ( $90^\circ$  and  $120^\circ$  jumps). For the mid-chain peroxy radical  $[-CF_2CF(OO^\cdot)-CF_2-]$ , the partial g-averaging in the ESR spectra could be fit well by chain axis rotation with  $90^\circ$  jumps, whereas the complete g-averaging observed at room temperature for the end-chain peroxy radical  $[-CF_2-CF_2-CF_2(OO^\cdot)]$  could be fit using a cubic jump model. An activation energy of 18.4 kJ/mol was found for the



end-chain peroxy radical motion.

17. Peroxy Spin Probe Studies of Motion In Methacrylate Copolymers And In Polypropylene Chains, D. Suryanarayana and Larry Kevan, J. Phys. Chem. 86, 0000 (1982).

Motional effects in methacrylate polymers, including poly(methylmethacrylate), poly(methyl- $\alpha$ -fluoroacrylate) and poly(methylacrylonitrile) and also in polypropylene (isotactic) have been investigated using peroxy radicals as spin probes. The ESR spectra of the polymer peroxy radicals were studied as a function of temperature from 77 to 370 K. The electron spin resonance spectra measured at both 9 and 35GHz revealed minor changes in the spectral line shapes. However, reversible  $g$  shifts in the  $g_{\parallel}$  component of the polycrystalline ESR spectra was observed over the entire temperature range. This  $g$ -shift has been attributed to the presence of motion in these polymers. Various motional models including chain axis rotation with  $90^{\circ}$  or  $120^{\circ}$  jumps, C-O bond rotation with  $180^{\circ}$  or  $120^{\circ}$  jumps, and a cubic jump process were considered. The experimental variation in the spectra were best fit with the C-O bond rotational model with the O-O group undergoing two successive  $180^{\circ}$  jumps for a COO angle of  $104^{\circ}$ . It appears that chain axis motion is minimal for these polymers due to steric hindrance of the side groups.

18. Peroxy Spin Probe Studies of Motion in Poly(vinylidene fluoride), D. Suryanarayana and Larry Kevan, J. Am. Chem. Soc., 104, 0000 (1982).

Motional effects in poly(vinylidene fluoride) have been investigated using peroxy radicals as spin probes to contrast with previous studies of peroxy radical motion in polytetrafluoroethylene and in polyethylene. The predominant radical formed by radiolysis at 77 K is  $-\text{CF}_2-\text{CH}_2\cdot$ . In the presence of oxygen this radical readily

converts to the peroxy radical  $-\text{CF}_2-\text{CH}_2-\text{O}-\text{O}\cdot$ . The electron spin resonance (ESR) spectrum of this peroxy radical was studied as a function of temperature from 77 to 360 K. The ESR spectrum measured at both 9 and 35 GHz revealed changes in the spectral lineshapes due to averaging of the  $g$ -anisotropy which is attributed to motion in this polymer. Various motional models including polymer chain-axis rotation, C-O bond rotation and a cubic jump process were considered. The experimental variation in the spectra are best fit with a C-O bond rotation model with  $180^\circ$  jumps for a COO angle of  $104^\circ$  in a temperature range between 77 and 280K. However, above 280 K extra lines between the  $g_{\parallel}$  and  $g_{\perp}$  regions of the spectra indicate that a cubic jump motional process dominates. This is presumably related to the greater freedom of motion at the higher temperature. The cubic jump motional process can be interpreted as a helical twisting motion of the end of a polymer chain.

19. ESR Characterization of The Dynamical Properties of Urea - n - Alkane Adducts Using Peroxy Spin Probes, D. Suryanaryana, W. Chamulitrat and Larry Kevan, J. Phys. Chem. 86, 0000 (1982).

The motional effects in urea adducts of n- alkanes, of chain size  $\text{C}_{12}\text{H}_{26}$  to  $\text{C}_{24}\text{H}_{50}$ , have been investigated using peroxy spin probes employing electron spin resonance (ESR). Temperature variations in the ESR spectra of the respective peroxy radicals of urea - n - alkanes were measured in the temperature range from 77 to 300 K. The ESR spectra at low temperatures ( $\sim 100\text{K}$ ) reveal an anisotropic  $g$ -tensor,  $g_{\parallel} = 2.037$  and  $g_{\perp} = 2.005$ , whereas at higher temperatures ( $\sim 200\text{K}$ ), the  $g$ -tensor is averaged to a new set of values,  $g_{\parallel}^r = 2.002$  and  $g_{\perp}^r = 2.021$ . The isotropic  $g$  value is constant for the entire temperature range. At intermediate temperatures the ESR spectra reveal "extra features between the  $g_{\parallel}$  and  $g_{\perp}$  regions which are characteristic of

peroxy radical motional effects. The spectral dependence with temperature has been successfully simulated using a chain-axis rotational model with  $120^\circ$  jumps for the entire temperature range employing the method of modified Bloch equations. The peroxy motion in urea - n - alkane adducts gives the following activation energies for the three-fold barrier:  $E = 6.8$  kJ/mol for urea - n-  $C_{12}H_{26}$  and  $E_a = 10.4$  kJ/mol for urea - n -  $C_{20}H_{42}$ . These values show the effect of chain length on the freedom of motion.

20. Study of Motional Effects In Poly(vinyl Alcohol) Chains by Analysis of Temperature Dependent Alkyl Radical ESR Spectra, D. Suryanaryana and Larry Kevan, J. Phys. Chem., 86, 000 (1982).

Temperature dependent electron spin resonance spectra of the  $\dot{C}H_2-COH-CH_2-$  radical in  $\gamma$ -irradiated poly(vinyl Alcohol) powder at 9.2 GHz have been measured between 298 and 385 K. The spectral changes have been successfully simulated by the modified Bloch equations using a two jump model with interconversion between axial and equatorial beta hyperfine splittings.

### 3. Scientific Talks Presented

- Army - T39 Application of Electron Spin Echoes and ESR Second Moment Analysis to the Determination of Matrix Structure Around Trapped Radicals in Disordered Systems, L. Kevan, P. A. Narayana, S. Schlick, M. K. Bowman, B. L. Bales and R. N. Schwartz, Twelfth International Symposium On Free Radicals, Laguna Beach, California, January 4-9, 1976.
- Army - T40 Future Research Trends on Electrons In Condensed Media, L. Kevan, Symposium on Radicals and Electrons in Condensed Media, Caracas, Venezuela, January 26-31, 1976. Invited Lecture.
- Army - T41 Electron Solvation Mechanisms, L. Kevan, Chemistry Seminar, Northern Michigan University, Marquette, Michigan, February 11, 1976.
- Army - T42 Matrix ENDOR Studies of the Orientation of Amine Molecules Around Trapped Electrons in  $\gamma$ -Irradiated Amine Glasses, F. Q. H. Ngo, S. Noda and L. Kevan, Fourth Symposium on Radiation Chemistry, Keszthely, Hungary, June 1-6, 1976.
- Army - T43 Solvated Electron Structure, L. Kevan, Seminar, Technical University, Todz, Poland, June 7, 1976.
- Army - T44 Solvated Electron Structure, L. Kevan, Invited Lecture, Polish Chemical Society, Warsaw, Poland, June 9, 1976.
- Army - T45 Geometrical Structure of Solvated Electrons, L. Kevan, Invited Lecturer, Annual Meeting of the Japanese Society of Radiation Chemistry, Kyoto, Japan, October 10-12, 1976.
- Army - T46 Application of Electron Spin Resonance to Radiation Chemistry I, Invited Lecture Series, L. Kevan, Nagoya University, Japan October 19, 1976.
- Army - T47 Application of Electron Spin Resonance to Radiation Chemistry II, Invited Lecture Series, L. Kevan, Nagoya University, Japan October 22, 1976.
- Army - T48 Application of Electron Spin Resonance to Radiation Chemistry III, Invited Lecture Series, L. Kevan, Nagoya University, Japan October 26, 1976.
- Army - T49 Localization and Solvation of Electrons in Condensed Media, L. Kevan, Invited Lecture Series, L. Kevan, Nagoya University, Japan October 26, 1976.
- Army - T50 Localization and Solvation of Electrons in Condensed Media, L. Kevan, Japan, Atomic Energy Research Establishment, Takasaki, Japan, October 27, 1976.

- Army - T51    Localization and Solvation of Electrons in Condensed Media, L. Kevan, Seminar, University of Tokyo, Japan, October 28, 1976.
- Army - T52    Localization and Solvation of Electrons in Condensed Media, L. Kevan, Radiation Center of Osaka Prefecture, Japan, November 30, 1976.
- Army - T53    Application of Electron Spin Resonance to Radiation Chemistry, Lecture Series, L. Kevan, Hokkaido University, Sapporo, Japan, January 21, 1977.
- Army - T54    Electron-Solvent Interactions, Invited Lecture Series of 12 lectures, L. Kevan, University of Paris-Sud, Orsay, France, May 7 - May 13, 1977.
- Army - T55    Localization and Solvation of Electrons in Condensed Media, L. Kevan, Center for Wave Mechanics, C.N.R.S., Paris, France, March 31, 1977.
- Army - T56    Known and Unknown Characteristics of Solvated Electrons, L. Kevan Seminar, University of Paris-Sud, Orsay, France, May 3, 1977.
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